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PbTe studied by 3D-ΔPDF analysis and ab-initio simulations

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PbTe is a leading thermoelectric material which complex and challenging structural properties have attracted significant interest in the last years [e.g. 1,2]. A pair distribution function (PDF) analysis based on neutron powder diffraction data suggested the emergence of fluctuating dipoles at temperatures higher than 100 K [1]. PDF peaks showed a large asymmetry and broadening with increasing temperature. This observation was interpreted as local symmetry lowering when warming up, which is a very unusual behavior. Subsequent experimental and theoretical studies have led to intense and in parts controversial discussions about the local structure of PbTe [2]. In this study, we attempt to shed light on the local structure of PbTe by combining the information from experimental single crystal 3D-ΔPDF analysis and ab-initio simulations.

High quality, temperature dependent diffuse scattering data between 125 K and 293 K were collected at the Swiss Light Source using a PILATUS 6M detector. The general appearance of the diffuse scattering does not change as a function of temperature, but the total diffuse intensities decrease with decreasing temperature. This can be interpreted such that only the amplitude, but not the spatial correlation of displacements is sensitive to temperature variation. The 3D diffuse scattering pattern was quantitatively analyzed with the 3D-ΔPDF modelling program YELL [3], resulting in an excellent agreement between observed and calculated data (see Figure). It was found that the strongest correlations between atomic displacements are along the <100> directions. In-phase displacements, similar to the behavior of acoustic phonons, dominate. On top, however, there is a clear significance for weaker anti-phase correlations, which, in analogy to optical phonons, induce local polarity. The complete 3D-ΔPDF analysis provides a detailed quantitative picture about the atomic pair correlations up to distances of about 60Å.

For obtaining complementary information, we performed ab initio molecular dynamics within the CP2K code using a 6x6x6 supercell of the conventional cubic cell. We first simulated and equilibrated the system in the isothermal-isobaric (NpT) ensemble at room temperature followed by a production run in the microcanonical (NVE) ensemble. When comparing the pair correlations extracted from the simulations to those obtained from the 3D-ΔPDF refinement we find an excellent match, i.e. the theoretical model is in very good agreement with the experiment. With this observation, we felt encouraged to also extract information from the simulated structure that is not directly accessible by diffraction: while the 3D-ΔPDF models are restricted to two-body correlations, the simulated structure delivers trajectories of all atomic coordinates of the simulated structure. This allowed us to extract a number of interesting many-body correlations, which will be presented in detail.

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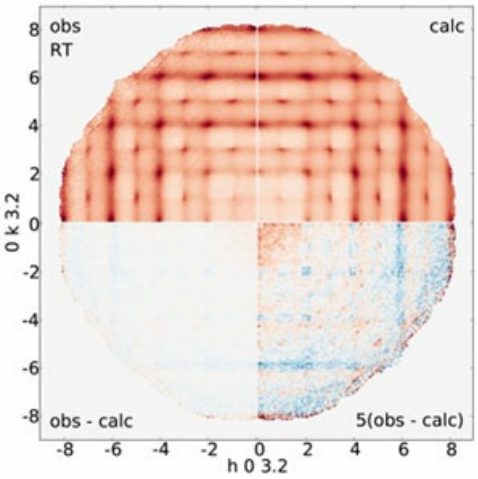

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